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HYDRIDE/OXIDATION (HYDOX) PROCESS FOR CONVERSION OF PLUTONIUM METAL TO OXIDE

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ABSTRACT

Options for plutonium disposition require PuO_2 that can be used as feed material for mixed oxide (MOX) reactor fuel pellets, or glass and ceramic immobilization forms (cf. Federal Register Doc. 97-1355, Vol. 62, No. 13, January 21, 1997). As part of a DOE-sponsored demonstration known as the Advanced Recovery and Integrated Extraction System (ARIES), conversion of plutonium to oxide by the Hydride/Oxidation (HYDOX) process will be used, along with other supporting technologies, to recover plutonium from the cores or "pits" of nuclear weapons that have been determined to be surplus to national defense needs. This demonstration will be performed jointly by the Los Alamos and the Lawrence Livermore National Laboratories at the Los Alamos Plutonium Facility.

The pyrochemical methods employed by HYDOX offer a simple and reliable process to recover plutonium in oxide form from various sources. This process will:

Separate plutonium from other nuclear and non-nuclear materials,

Convert massive metallic shapes into fine oxide particles,

Produce oxide directly acceptable for MOX fuel fabrication, and

Produce no solid or liquid waste.

The paper describes the reactor module and operational sequences, provides up-to-date experimental results, identifies rate-controlling factors, and discusses their impact on the reactor design.

1. INTRODUCTION

The removal of plutonium from pits by hydriding, and converting the hydride back to metal was a process for

which prototypical equipment was fabricated and demonstrated at LLNL, as part of the DOE Complex 21 effort. Due to high efficiency, selectivity and the elimination of solid and liquid wastes, the process came to be viewed as baseline for removal and consolidation of plutonium from pits. The LLNL system, known as HYDEC (hydride/dehydride/casting), has worked very well. With the inception of the Fissile Materials Disposition Program (FMDP), it became clear that not only did plutonium need to be removed from pits but that conversion to oxide was required for most disposition options. LLNL proposed using hydriding technology to remove plutonium from pits and then conversion of the hydride to oxide.

In the summer of 1995, a proposal was submitted to the FMDP program to fast track the main components of a pit disassembly and conversion line (ARIES). Project objectives at that time were to rapidly develop (in less than two years), deploy and demonstrate the ARIES line in a transportable system. LLNL assumed responsibility for the pit bisection and hydride/oxidation (HYDOX) modules. Since the HYDOX module required the greatest development effort, LLNL elected to meet project schedule requirements by adapting the prototype HYDEC system to the HYDOX process. Concurrently, various reaction options were examined in order to establish process operational parameters.

In FY96, the studies were conducted on a small scale non-prototypical system with the hydriding done in a separate vessel. The following options were examined:

Option 1 - hydride Pu metal, dehydride to metal powder, and convert the metal powder to oxide.

Test results: the dehydriding step was very slow at temperatures below the sintering point of plutonium metal. This would result in extremely long process times (several days).

Option 2 - hydriding followed by conversion of the hydride to oxide using 4% oxygen in inert gas (two step). In FY96 this was designated as the baseline process.

Test results: The low oxygen concentration used to maintain a product gas with safe level of hydrogen could not be offset with higher gas flow rates to speed up the reaction due to particle elutriation from the bed. A fixed bed reactor required low flow rates yielding long process times (several days). Initially, argon was used as the inert gas. This led to local overheating of the bed. At temperatures greater than 600°C partial dehydriding could occur. Helium was substituted for argon which improved bed temperature control but still resulted in long process times.

Option 3 - hydride only a small amount of plutonium metal and then feed pure oxygen which will react with the hydride, releasing the hydrogen for further hydriding (cyclic).

Test results: The oxidation of the hydride required the temperature of the part to be about 400°C which produced massive hydride and very large oxide pieces. The process required more hydrogen than desired to ensure that any potential energetic reaction would not compromise the vessel integrity.

Option 4 - hydride the metal, nitride the hydride, and oxidize the nitride (three step).

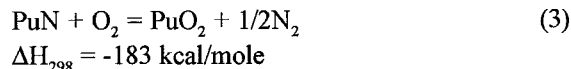
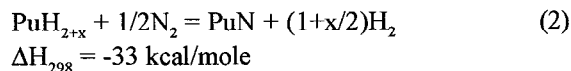
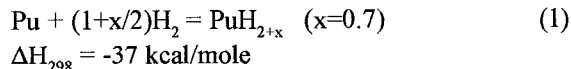
Test results: Only a few tests were performed in FY96. These tests did show that a fine powder product could be obtained in a shorter time than in the two-step process with no particle elutriation. However, due to the exothermic nature of the nitride to oxide conversion, the flow rate of oxygen had to be controlled to minimize bed overheating. When the bed was allowed to exceed temperatures of 800°C, some bed sintering was observed. The oxide would have required additional grinding to meet MOX fuel requirements.

At the end of FY96 a decision was made to further develop the three-step process and examine methods of improving heat transfer within the bed. The prototype HYDOX upgrade of the LLNL HYDEC unit was designed and installed. Since November 1996, the LLNL HYDOX unit (85 mm diameter crucible) has been in continuous operation. While initial demonstrations of the 2- and 3-step processes produced oxides with bulk densities of approximately 3 g/cc, in October of 1996, some of the 3-step development runs produced oxides with bulk densities of 1.5 to 2 g/cc. The 85 mm crucible appeared too small to accommodate the desired amount of plutonium. LLNL and LANL concurred that the crucible size should be increased to 120 mm. The ARIES HYDOX demonstration unit was designed and built with a 120 mm crucible. The LLNL unit was upgraded to 120 mm later in FY98.

The three-step conversion methods described below are part of the ongoing experimental study in Livermore aimed at identifying a strategy leading to the shortest conversion cycle.

2. PROCESS CHEMISTRY AND EQUIPMENT

The plutonium conversion process is based on the following reactions:



In the first step Pu metal is hydrided at 25-400°C and 20-200 torr H₂ pressure as described by reaction (1). The spalling hydride is collected in a quartz crucible.

In the second step the plutonium hydride is nitrided as described by reaction (2), following an elevated vacuum sequence, to ensure the absence of residual hydrogen. Since no hazardous gas mixtures occur in this step, the feed is pure N₂ and the bed temperature is maintained at or below 600°C (to avoid dehydriding) by nitrogen flow control.

In the third step the plutonium nitride is converted to plutonium oxide as described by reaction (3). This step is usually the most time-consuming due to the high heat of reaction and extremely low thermal conductivity of PuO₂. Again, since no hazardous gas mixtures are involved, the feed gas may be pure O₂. The bed temperature is maintained at or below 800-900°C (to avoid fusing) and controlled by the oxygen flow.

The prototype HYDOX unit is shown in Figs. 1 and 2.

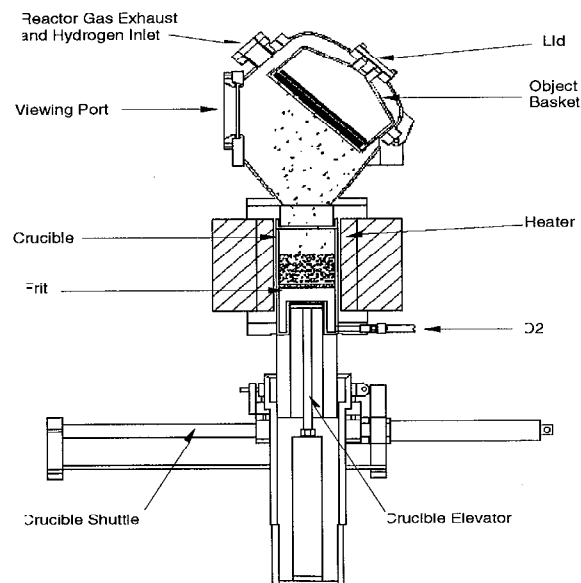


Fig. 1. Diagram of HYDOX reactor module.

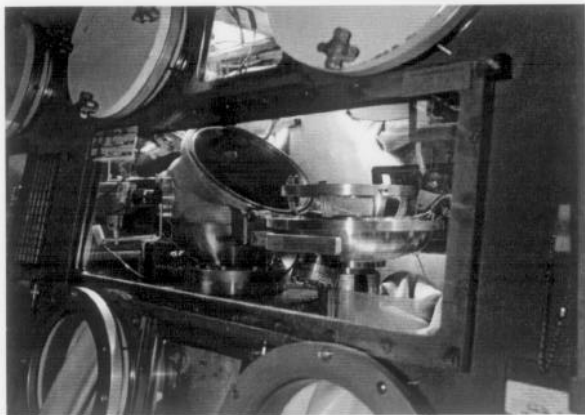


Fig. 2. HYDOX unit inside the glovebox.

3. 85 MM CRUCIBLE AND UP FLOW OXIDATION

In FY97 all HYDOX runs were conducted in an 85 mm quartz crucible with oxygen and/or nitrogen gas fed from under the crucible frit as shown in Fig. 1. Flowing upward gases reacted with the bed material. In this arrangement, the upper limit for the total gas flow was set to 1 liter/min (STP) to control particulate elutriation. In practice, that restriction applied only to the 4% oxygen-helium mixture used in two-step conversion method. In the three-step approach, which allowed the use of pure nitrogen and oxygen, the gas flow was limited by the bed temperature, usually well below 1 liter/min. The results of the FY97 runs are summarized below.

3.1 Hydriding

With high purity hydrogen, the hydriding starts at room temperature after a brief (few minute) induction time. Once started, the reaction is vigorous and capable of quickly raising the Pu part temperature to several hundred degrees C, necessitating control via the hydrogen flow rate. For the optimum hydride sizes, and the bulk density on the order of 4.0 g/cc the H_2 feed rate has to be within 1.5 to 2 SLPM, usually at 30 to 50 torr hydrogen pressure. It takes 1 to 1.5 hours to convert 1 kg of plutonium to $PuH_{2.7}$. When the hydrogen is not pure, additional time is required. It has been observed that a 10 min induction time with 60 ppm moisture in hydrogen increases to 300 min if moisture content increases to 600 ppm. Similarly, if oxygen is present in the hydrogen, much higher hydrogen pressure (sometimes exceeding our maximum allowable pressure of 500 torr in the HYDOX unit) may be required to maintain a satisfactory hydriding rate. Likewise, even a few percent of argon in hydrogen (e.g., an argon leak from glovebox into the HYDOX unit) caused a similar

effect. Most hydriding runs averaged 1.5 to 2 hours per 1 kg of Pu (including the induction time).

3.2 Nitriding

Due to only a moderate heat generation rate, the temperature control of nitriding is relatively simple. After initial electric furnace preheating of the bed to 450°C, the nitrogen feed is turned on. Once the pressure in the chamber reaches 500 torr, nitrogen flow is adjusted to maintain the bed at 500 to 600°C with the furnace turned off. At this temperature nitrogen consumption is nearly 100% efficient. It takes an average of 3 hours to nitride 1 kg of $PuH_{2.7}$ with pure nitrogen at 500 torr pressure. Once a stoichiometric amount of nitrogen has been fed, the bed temperature begins to fall. The furnace is turned on to keep the bed temperature at 600-650°C. The nitrogen feed is then shut off and the chamber evacuated to assure dehydriding of any unreacted hydride.

3.3. Oxidation of nitride with pure oxygen

Oxidation releases 4.5 times as much heat (per mole of Pu) as nitriding. Furthermore, PuO_2 has a much lower thermal conductivity than either the hydride or nitride. Slow heat transfer across the stationary bed tends to distribute heat unevenly and creates hot spots. This puts a severe restriction on oxygen flow and, therefore, on process speed. Typical oxidation time with pure oxygen is 17 hours per kg of PuO_2 when the bed temperature is limited to 700°C. PuO_2 powder obtained under such conditions has a bulk density of 1.5 to 2.0 g/cc and is extremely fine, with 15 μm median size and over 6 m^2/g specific surface area.

With oxygen utilization being close to 100%, the process control is similar to that of nitriding. Once a stoichiometric amount of oxygen has been fed, the bed temperature begins to fall. The furnace is turned on to keep the bed temperature at 600-700°C. An additional 5 to 10% oxygen (to assure complete conversion) is passed through the bed before the oxidation cycle is complete.

Since the steps involving hydrogen and oxygen are separated, the three-step process is inherently safe and, as such, readily amenable to modifications. Among the process improvements which led to a reduction of processing time by a factor of 4 to 5 were the combining of hydriding and nitriding in a single "cyclic" step, dilution of oxygen with helium and flow reversal, and increasing the crucible diameter from 85 mm to 120 mm.

4. CYCLIC HYDRIDE/NITRIDING

The process in its present form involves partial hydriding using a small quantity of hydrogen followed

by the cyclic hydride/nitriding during which only nitrogen is fed to the reactor. As nitrogen reacts with the hydride, it liberates the hydrogen which hydrides more Pu metal. Thus the small initial quantity of hydrogen is recycled until all Pu has been converted to PuN. After brief heating and evacuation (to assure a hydrogen free reaction zone) the final oxidation step completes the Pu conversion process.

As in ordinary hydriding, the HYDOX vessel is sealed through most of the cyclic run. Therefore, the progress of the reaction in the cyclic process can be followed as precisely as in ordinary hydriding by observing the total amount of nitrogen fed to the reactor. Low pressure (<50 torr) during most of the process is an indicator that both the hydriding and the nitriding steps of the cycle are proceeding normally without interfering with one another. Under normal conditions the pressure rises when all plutonium metal has been converted, because there is nothing left for the hydrogen to react with. These conditions are defined by the initial Pu mass, the initial H₂ quantity, and the nitrogen equivalent of hydrogen required to complete ordinary hydriding. Once that equivalent amount of nitrogen has been fed, causing the pressure to rise, the vacuum exhaust valve is opened allowing unused hydrogen to escape and permit completion of nitriding. The minimum additional nitrogen to be fed is the difference between the amount already fed and the stoichiometric requirements.

The smaller the Pu part, the higher the temperature it can attain during the brief initial period of hydriding. At high enough temperature a substantial fraction of hydride will react with nitrogen directly on the part, further raising the part temperature and accelerating the nitriding reaction. Yet thermodynamically the process appears to be stable since, in the vicinity of the Pu melting point (640°C), dehydriding is favored over hydriding. An impeded hydriding would hold back the nitriding part of the cycle until the part temperature returns to the range favoring hydriding.

In practice, slowdowns, as mentioned above, are unlikely, and the cyclic process is usually fast and steady. Another built-in control mechanism, radiation heat loss from the exposed part, is responsible for stabilizing part temperature around a nearly ideal 400-500°C at high process rates. At this temperature the material spalling into the crucible is largely nitride. Since a bed with little hydride cannot generate enough heat to maintain the 400-500°C required for nitriding, additional heat is provided by the furnace. With heat removal no longer a limiting factor, the cyclic process is substantially faster than either hydriding or nitriding alone. An additional benefit is the trivial amount of hydrogen inventory which, if leaked to the glove box, would result in glovebox concentrations below the flammability limit, even if the glovebox atmosphere was compromised.

5. 120 MM CRUCIBLE AND DOWN FLOW OXIDATION

To mitigate uneven temperature and associated hot spots in the bed during oxidation, helium, a high thermal conductivity inert gas, was added to the oxygen. To control particle elutriation and dusting caused by sharply increased gas flow, its direction was reversed from upward to downward.

Seven runs, initially using an 85 mm quartz crucible, were conducted in which PuN was oxidized using downflow (up to 7 liters/min) through the bed.

In order to maintain, with the furnace turned off, a constant 700-800°C temperature in the central part of the bed throughout the run, the initial 10% oxygen concentration in the feed was gradually increased to 100% by the end of the run. The temperature near the crucible wall was 200°C lower than the central part of the bed. The temperature control was easy and straightforward. While higher resistance through the compressed bed caused gas to partially bypass the bed, the higher, in absolute terms, oxygen flow rate more than compensated for the loss. As a result, the net oxygen consumption rate increased, bringing the oxidation time to around 7 hours per 1 kg of Pu. The process produced very fine particles of PuO₂ with an average bulk density of 2.3 g/cc, comparable to that from the three-step process using pure oxygen.

Over the last year, the HYDOX reactor underwent some modifications. In order to accommodate larger quantities of PuO₂ powder, the crucible diameter has been increased from 85 to 120 mm, doubling its volume and cross section area. After extensive material testing, 120 mm metal (Hastelloy X) crucibles are being used as a possible replacement for the quartz crucibles. The crucible seals have been redesigned to improve dust control and to prevent any gas bypassing.

The control system and instrumentation have also been modified and became, under a LabView interface, fully integrated. The result is a comprehensive and flexible computer control system covering all major and auxiliary HYDOX steps. Once the Pu Facility re-opened in April, 1998, four process runs conducted under the new control system confirmed its logic, reliability, and ease of updating as new information or ideas became available. At the present, a relatively straightforward oxidation step can be conducted without operator intervention yielding more consistent results than was before possible. For the much more complex cyclic hydride/nitriding step the optimization algorithms for automatic operation have been written but not yet tried.

The four PuN oxidation runs have been conducted at elevated temperatures of 850°C to 950°C in 120 mm quartz and metal crucibles using downflow of an oxygen/helium mixture at up to 15 liters/min. The

results clearly indicate that the oxidation time is a function of temperature and the total O₂-He flow. The oxidation rate varied from 3 hours per 1 kg of Pu at 850°C to 1.5 hours per 1 kg of Pu at 950°C, although the latter temperature produced a visibly coarser product. The product obtained at 850°C was visibly finer, however sieving revealed that it did not meet the ASTM specification requiring 100% of the powder to be less than 100 µm. Consistent with the material coarseness, its bulk density varied from 2.4 g/cc at 850°C to 3.0 g/cc at 950°C.

Given the proposed grinding option prior to MOX fabrication, the powder size may not be an issue. Otherwise, the oxidation temperature will have to be reduced, with perhaps only little (if any) increase in oxidation time. Our thermal analysis indicated that about 70% of the oxidation heat in downflow mode is removed through the crucible bottom frit. Doubling the frit area was thus another significant factor in reducing oxidation time from 7 hours per 1 kg of Pu at 800°C in a 85 mm crucible to 3 hours per 1 kg of Pu at 850°C in a 120 mm crucible. Furthermore, the frit of the new 120 mm crucible was unintentionally cooled with a blower installed to prevent overheating of the teflon-lined downflow exhaust hose. Therefore the effect of a dedicated frit area cooling on oxidation time needs further evaluation.

6. FUTURE DEVELOPMENT

6.1. ARIES Project (new HYDOX unit with 120 mm metal crucible)

- Exploring forced cooling of the crucible bottom as a means of reducing oxidation time.
- Fine tuning of oxidation temperature to minimize processing time while meeting powder specification.
- Fine tuning cyclic process to insure Pu removal selectivity in the presence of other hydridable metals.
- Test process optimization algorithms for unattended HYDOX operation.
- Establish operational parameters and cycle time for the remaining ARIES weapons parts and finalize process control options prior to ARIES demonstration.
- Support of initial ARIES demonstration and continued engineering demonstrations at LANL.

6.2. Plutonium Immobilization Project

- Continue design, development and testing of the fluidized bed two-reactor HYDOX system for

converting Pu alloys and ZPPR fuel to oxide for immobilization.

- Use existing HYDOX unit to explore cyclic process adaptability for various feed materials and determine which (if any) feed types need to be processed in separate steps.
- Examine alternate gallium removal technologies and incorporate gallium removal into the second stage of the two-reactor HYDOX system. LLNL intends to take full advantage of this development by designing the system to be capable of processing pits in support of the Pit Disassembly and Conversion Program.
- Develop automated control and remote handling in the HYDOX operation for high activity material.

7. CONCLUSIONS

- A <4 hours per 1 kg of Pu conversion time has been demonstrated for the HYDOX process.
- The three-step process is capable of producing oxide suitable for MOX fuel fabrication.
- Separation of hydrogen from oxygen in the three-step approach eliminates restriction on oxygen concentration (4% O₂ in inert gas is required for two-step process).
- Combining hydriding and nitriding in a cyclic process further reduces processing time and greatly reduces the hydrogen inventory.
- The process can be run with 10-20 liters of H₂, which, even if leaked to the glove box, would result in a safe concentration <4%.

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